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(54) Oriented polymeric films, packaging made from such films and methods of making the films and packaging.

(57) Molecularly oriented plastic films have five layers simultaneously molecularly oriented. The films are made by coextruding and have a first layer which provides a barrier to gaseous transmission through the film and has a composition of 0% to 50% nylon or nylon copolymer, and 50% to 100% ethylene vinyl alcohol. Second and third adhesive layers are each adhered to a respective one of the surfaces of the first layer, and have compositions comprising olefinic polymers, copolymers or blends thereof, the compositions all having carboxyl modifications therein. Fourth and fifth layers are respectively adhered to the second and third layers on their respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 0% to 60% linear low density polyethylene. After extruding the films, they are heated to molecular orientation temperature and are stretched, for example using the gas bubble technique when the film is extruded through an annular die. Heat sealable bags of pouch form are made from juxtaposed sheets or portions of film, or from a film of tubular form, by one or more peripheral heat seals as appropriate, leaving the bag open along one part of its periphery for filling and subsequent closure by a heat seal.

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"ORIENTED POLYMERIC FILMS, PACKAGING MADE FROM SUCH FILMS AND METHODS OF MAKING THE FILMS AND PACKAGING"

The present invention relates to oriented polymeric films, packaging made from such films and methods of making the films and packaging.

It is conventional to utilize films of various oriented polymeric materials for the packaging of foods and other consumer products. Although the necessary and desirable properties depend upon the specific applications for which the films are intended, normally they should exhibit good uniformity, strength, toughness, abrasion and flex-crack resistance, gloss, and heat stability. When formed into closed and sealed packages, such as by heat sealing, the packages should exhibit high burst strength and resistance to cutting, such as by metal closure clips. Also, because of the susceptibility of many food products to deterioration upon exposure to oxygen, it is often imperative that the film employed exhibit good barrier properties.

As is also well known, it is common practice to package meat and other food products in molecularly oriented films that can be shrunk upon exposure to heat. The need for good strength characteristics is particularly acute in such instances because of

the vulnerability of the film to damage under the conditions of use.

Generally, the combination of characteristics necessary to provide films that are suited for use in many packaging applications is not possessed by a single layer product, and hence numerous multiple layer films have been developed or proposed.

Both the film producer and the film user require that oriented films satisfy a multiplicity of requirements. Of primary importance to the film user, in the case of shrink films, is the capability of the film to survive physically intact the processes associated with the film as a package, as it is filled, evacuated, sealed closed and heat shrunk. The film package must also be strong enough to survive the material handling involved in moving the contained product, which may weigh 100 pounds (45.4 kg) or more, along the distribution system to the next processor or to the user. Thus the package must physically protect the product.

It is often desirable to the film user that the package film serve as a barrier to infusion of gaseous materials from the surrounding environment. Of particular importance is provision of an effective barrier to infusion of oxygen, since oxygen is well

known to cause spoilage of food products. The package should also be clear to be visually appealing and permit inspection of the product.

The film producer requires a film which can be produced competitively while meeting the performance requirements of the user. Thus the film materials should be readily extrudable, and susceptible to orientation, with sufficient leeway in process parameters to allow for efficient film production. The process should also be susceptible to efficient extended production operations. In the orientation process, the film must be able to withstand the stretching. The orientation temperature should be a temperature which is economically achieved by the producer. Moreover, the orientation should provide for use of economical shrink processes by the film user.

Conventional shrink films are often produced and used as bags and have generally been constructed with ethylene vinyl acetate (EVA) and an oxygen barrier layer such as Saran (Registered Trade Mark) or ethylene vinyl alcohol (EVOH).

Notwithstanding its advantages, shrink film packaging, and particularly shrink bag packaging of meat, is not without its difficulties, many of which

are attributable to limitations inherent in the films utilized for such applications. As will be appreciated, the processes of stretching the film, and later shrinking it, subject the film to rather severe conditions, due to the nature of the operations.

It is especially important to appreciate that the film is particularly vulnerable to failure under the conditions of operation due to the relatively high temperatures to which it is subjected in the orientation and shrinking processes.

The film must be susceptible to orientation without distortion and without separation of the multiple layers, which are normally present in films of this nature. The film must be strong enough, at the orientation temperature to withstand the stretching without the creation of holes, tears, or non-uniform zones of stretching. In the case of blown tubular film, as in the well-known double bubble process, the film must be capable of physically supporting the stretching bubble during the orientation process. Finally, each of the layers of the film should be susceptible to orientation in the multiple layer film without fracture, separation, or creation of holes.

In shrink packaging use, the film must respond

to heat rapidly enough for commercial practicality, and yet must not exhibit such a level of shrink energy as would cause the film to pull apart or delaminate during shrinkage, under its own internal forces. Moreover the shrink related problems may be seriously increased, for example, when the film is to contain a cut of meat which includes protruding bones and/or significant depressions in its surface.

Prospective films are conveniently subjected to preliminary testing in a laboratory. In one such test, the prospective film is formed into packages by means of heat seals and air is injected into the packages. The recorded parameter is the air pressure that a given package successfully holds without failure of its sidewalls or the seals. Another convenient laboratory test measures the interlayer adhesions at the layer interfaces, by pulling apart the layers and measuring the pulling force required. The ultimate goal, of course, is to produce a sealed package, containing the contemplated product, and to have the sealed package retain its integrity as a sealed unit throughout the distribution and sale of the product, to the time of opening by the ultimate user.

In the uses contemplated for oriented films to which the present invention is directed, the most severe conditions normally encountered by the films will be those associated with the overall process of a packager. In the packaging process, films may be made into containers, the containers filled with a product and sealed closed, and may also be evacuated and/or heat shrunk. The most significant test would be to use the films in the commercial processing operations of a packager, to ascertain the overall reduction in the percentage of packages which leak.

Certain available 3-layer films having a Saran layer are disclosed in US-A No. 4,247,584. These films provide a good balance of properties. Saran, however, poses several problems. It has a brown color, which is generally undesirable. During extended extruder operation, bits of carbon form from decomposition of the Saran in the extruder equipment, and later pass out through the die as undesired inclusions in the extruded film. As a result, the operation must be shut down periodically for die cleaning. Further, the power required to extrude Saran is relatively high. Thus, while Saran is accepted as a functional material,

alternative barrier materials would be desirable.

It is also suggested in the said US-A No. 4,247,584 that a barrier layer of EVOH could be used instead of the Saran layer, so as to provide the excellent oxygen barrier properties of EVOH while avoiding the disadvantages of Saran. EVOH does have certain problems associated with its fabrication and use, but in certain applications it may be advantageously used. In improvements on the technology of oxygen barrier materials, oriented blends of EVOH are proposed in copending unpublished US patent applications Nos. 290,171 and 290,172 both assigned to us. The first US application discloses oriented films of blends of EVOH and nylon along with plasticizers for the nylon, and the second discloses oriented films wherein EVOH is blended with any member of a family of polymers.

In our pending, presently unpublished European Patent Application No. 83 30 0831.1, it is proposed that the inclusion of linear low density polyethylene (LLDPE) in at least one of the layers provides a significant decrease in the leaker rate when film bags are used for shrink packaging of meat.

While the art of oriented multiple layer films is becoming crowded, there still exists a deficiency,

leaving unfulfilled a need for easily produced oriented films which exhibit the afore-mentioned desirable properties. Particularly, there remain certain problems concerning the strength of the film and packages made therefrom and the adhesion of the layers to each other at the layer interfaces, in addition to the typical problems of incompatibility of certain polymers with orientation. Thus it is desired to provide a film having improved strength properties imparted generally by creating a film having the desirable characteristics and imparting thereto properties of improved interfacial adhesion, and attendant improvements in the overall strength properties of such films as demonstrated in laboratory tests and in commercial use.

It has now been found that certain improvements are achieved in an oriented film which, according to the present invention includes:

(a) a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol;

(b) second and third adhesive layers each adhered to a respective one of the opposite

surfaces of the first layer, the second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and

(c) fourth and fifth layers adhered to the second and third layers on the respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene;

the said layers each having been stretched in molecular orientation to substantially the same degree, and the said layers being adhered to each other directly at the respective interfaces without the use of additional adhesive materials;

the oriented film being susceptible of being made into a closed and sealed container or bag by means of heat seals formed along terminal edges of adjacent superimposed sheets or portions of the film.

The oriented film is susceptible to being made into a closed and sealed container by means of one or more heat seals formed (as appropriate) about the periphery of adjacent superimposed sheets.

The resulting container and its seals are capable of withstanding a high static internal gaseous pressure, up to at least as high as 29 pounds per square inch gauge (2 bar).

In some of the preferred structures the composition of the first layer is 30% to 50% nylon and 70% to 50% EVOH. An especially preferred composition for some structures is 40% nylon and 60% EVOH. In other structures it is entirely acceptable that the first layer is essentially 100% EVOH. A small residuum of EVA is also present as unused reaction component from the hydrolysis of EVA to EVOH.

The invention also provides a method of making a five layer oriented polymeric film, wherein the film includes a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol; second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and fourth and fifth layers adhered to said second and third layers on their respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene; and

wherein the method comprises the steps of:

(a) coextruding the five layers as a five layer film;

(b) cooling the film;

(c) reheating the film to molecular orientation temperature;

(d) molecularly orienting the film; and

(e) cooling the molecularly oriented five layer film;

the oriented film being susceptible to being made into a closed and sealed container by means of heat seals formed along terminal edges of adjacent superimposed sheets or portions of the film.

The coextrusion may be performed through a narrow straight slot die to form a flat sheet such as by cast coextrusion. Another means of forming the film is by coextruding it through a circular die to form a tube as by tubular extrusion, blown film extrusion, or water quenched tubular extrusion.

Where the film is formed as a flat sheet, orientation may be achieved as by compression rolling, by stretch orientation between a pair of nip rolls or by a tentering orientation process.

Where the film is produced in tubular form, its orientation is preferably effected by forming a bubble between two pairs of nip rolls and controlling the amount of orientation according to the amount of gas trapped in the bubble and by driving the nip rolls at different speeds as desired, to create longitudinal stretching of the film as well as the transverse stretching incurred primarily by the gas entrapped in the bubble.

Particularly where the film to be produced is tubular and where the tube is to be inflated or oriented in tubular form, it is desirable that the fourth and fifth layers include at least 10%, and preferably 25% to 40% LLDPE as a blend material with EVA.

The selection of the specific compositions of the adhesive materials for the second and third layers depends to some extent on the compositions of the first, fourth and fifth layers, and on the processing conditions, including the coextrusion and orientation processes. It is necessary that the second and third layer compositions include carboxyl modifications. Exemplary of these modifications are organic acids and anhydrides. Preferred materials are olefinic, of which specific examples

are low density polyethylene (LDPE), medium density polyethylene (MDPE), EVA, and LLDPE, all having the recited carboxyl modifications. Blends of modified olefins may also be advantageously used.

The invention further comprehends a bag for closing and sealing, as well as a filled bag when closed and sealed. Accordingly, the invention provides a fabricated plastics container or bag having an opening on one edge thereof, the bag having been fabricated from an oriented film comprising five polymeric layers, including:

(a) a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol,

(b) second and third adhesive layers each adhered to a respective one of the surfaces of the first layer, the second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and

(c) fourth and fifth layers adhered to said second and third layers on the respective surfaces opposite said first layer, the fourth and fifth layers comprising 40% to 100%

ethylene vinyl acetate and 60% to 0% linear low density polyethylene;

the said layers each having been stretched in molecular orientation to substantially the same degree, and the said layers being adhered to each other directly at their interfaces without the use of additional adhesive materials; and the bag being susceptible to being made into a closed and sealed container by means of a heat seal along the said opening.

The invention also provides a method of fabricating a plastic bag having an opening on one edge thereof susceptible of closure by heat sealing, the remainder of the periphery of the bag having been closed as appropriate by one or more heat seals to form an open ended pouch, the said bag being fabricated from an oriented film which includes a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol; second and third adhesive layers adhered to respective surfaces of the first layer, the second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and fourth and fifth layers adhered to the second

and third layers on their respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene; and the method including the steps of:

(a) coextruding the five layers as a five layer film;

(b) cooling the film;

(c) reheating the film to molecular orientation temperature;

(d) molecularly orienting the film;

(e) cooling the molecularly oriented five layer film; and

(f) forming one or more heat seals as appropriate at the periphery of said bag except along the said one edge.

The fabrication of the bag from the film is most easily accomplished when the film is

extruded and oriented as a continuous tube. The bag is formed by severing a length of the tubular film, across its transverse dimension, from the continuous tube. The severed portion is essentially a collapsed cylinder with both ends open. The fabrication of a bag is completed by forming a heat seal across one end of the collapsed cylinder. The other end is left open for loading of product. When the product has been loaded, the bag is then evacuated, a clip is put in place on the unsealed end, and the bag is heat shrunk. Alternately the final closing seal may be made by, for example, a separate heat sealing process.

The invention will now be explained in more detail in the following non-limitative description of preferred embodiments thereof.

Each of the five polymeric layers in films according to this invention must satisfy certain specific functional requirements as described hereinafter. The first layer, generally known as the core layer has to layers on each of its surfaces, such that, in traversing through the thickness of the film from either outside surface, two other layers are traversed before the first or core layer is encountered. The composition of the first layer is selected to provide functional packaging properties, that impede oxygen transmission through the film, and lend toughness to the layer, particularly in the plastic state, to facilitate handling of the film during film production. It will be appreciated that desirably the composition of each layer imparts some degree of toughness to the film for ease of film production. The thickness of the first layer and of the previously-designated fourth and fifth layers (or outermost layers), however, cause them to be the layers most susceptible to improvements in toughness by proper selection of polymer composition, so usually these are the

layers for which such improvements are sought.

THE FIRST LAYER

The first or core layer includes therein at least 50%, and preferably at least 60% of an EVOH. The amount of EVOH in the first layer determines to a significant degree the overall effectiveness of the film in impeding transmission of oxygen. While as little as 20% EVOH in the first layer does improve the oxygen transmission rate over a nylon composition without EVOH, it is usually desirable to have at least 50% EVOH in the composition to realise the superior oxygen barrier property generally associated with EVOH. Therefore, 50% EVOH represents a preferred lower limit to the amount of EVOH. Higher levels of EVOH are advantageously utilized. While up to 100% EVOH is acceptable for the purposes of the invention, little added benefit of oxygen transmission barrier is achieved at levels of over 70% EVOH, and 60% EVOH is generally believed to provide the most efficient usage. The EVOH typically has a molecular weight in the range of abour 20,000 to 30,000 and a melting point temperature of about 325^{o} to 375^{o} Fahrenheit (163^{o} to 191^{o}C), these characteristics corresponding roughly to melt indices of about 9 to 1.5. The melt index values herein are determined in

accordance with ASTM Test D-1238, Procedure E or L, using a weight of 2160 grams and temperature of either 190° or 210° Centigrade, as appropriate. Typically, the EVOH has a density of 1.1 to 1.2. A suitable processing temperature for the EVOH is about 400° to 480°F (204° to 249°C) and preferably 410° to 440°F (210 to 227°C). While the degradation temperature of EVOH is generally regarded to be about 450°F (232°C), this is not inconsistent with the higher processing temperatures proposed herein, due to the short residence time at those temperatures in the extrusion process. Illustrative of EVOH resins that are suitable for use are those available from Kuraray and from Nippon Gohsei, both of Japan. The products of the former company are EP-E and EP-F, and those of the latter company are designated SOARNOL-D, SOARNOL-E, and SOARNOL-ET. EP-E and EP-F contain about 55% and 68% vinyl alcohol, respectively, in the molecule and have melt flow values, as determined at 190°Centigrade, of 5.8 and 1.5 respectively. SOARNOL-D, SOARNOL-E and SOARNOL-ET contain 71%, 62% and 62% vinyl alcohol, respectively, and exhibit melt flow values of 7.4, 8.0 and 3.5, respectively, as determined at 210° Centigrade.

After accounting for the presence of the EVOH,

the balance of the composition of the first layer is a plasticized nylon. The inclusion of nylon generally imparts the property of toughness, while reducing the amount of the more expensive EVOH which is used. Structural properties of improved toughness of the first layer composition as compared to 100% EVOH are discernible with as little as 10 weight percent nylon, based on the total layer composition. However, it should be appreciated that the incorporation of nylon in virtually any concentration is generally of some benefit, in improving orientation processing as well as enabling cost reductions to be realised.

A surprising feature of the films of the invention resides in the fact that as much as 30 weight percent nylon can be included in the blend composition of the first layer without reducing the effective oxygen barrier properties of the EVOH resin significantly. This has been found to hold generally true regardless of the nature of the nylon used, or of any additives which may be incorporated into the nylon.

While the polycondensation resins such as nylon 66 may be employed to advantage, for most purposes the addition polymer nylon 6 is preferred. To be suitable for such use, the nylon generally has a molecular weight in the range of 20,000 to 30,000

and a melting point temperature of about 415° to 440°F (213 to 227°C), with a melting point temperature of about 428°F (220°C) being optimal in many cases. Such nylon resins are normally processed at temperatures of about 510° to 540°F (266° to 282°C). This presents a fundamental difficulty, having regard for the EVOH, which is addressed in our pending European patent application No. 64330. As taught therein, the provision of a nylon/EVOH blend which can be extruded at temperatures below the degradation temperature of EVOH is achieved by the incorporation into the composition of an agent that serves as an effective plasticizer for the film-forming nylon. While some of the agents utilized may not previously have been regarded as plasticizers, in the present blends of the first layer herein, they do appear to perform that function. It appears that the plasticizing agents are capable of intermolecular hydrogen bonding and disruption of crystallinity within the nylon structure, to effectively lower the temperature at which processing can be carried out. As a result, film-forming nylons that normally process at temperatures of about 510° to 540°F (266° to 282°C) become processable at temperatures that are

considerably lower and that are, in fact, within a range of temperatures at which the EVOH is also processable and not subject to significant degradation. More particularly, the externally plasticized film-forming nylon resins, so plasticized, are processable with the EVOH resins at temperatures of about 400° to 480°F (204° to 249°C) with preferred temperatures being about 410° to 440°F (210° to 227°C).

The amount of plasticizer used may vary between fairly wide limits. As little as 2 percent or as much as 25 percent, based upon the weight of the nylon resin, may be acceptable. For satisfactory results, it will usually be necessary to use a concentration of plasticizer in excess of 2 percent, and 5 weight percent usually represents a preferred lower limit for such blends. Amounts of plasticizer in excess of 15 weight percent normally produce little added benefit, insofar as processing is concerned and therefore that concentration represents a preferred upper limit. The amount of plasticizer utilized in any given case, of course, depends upon a number of factors, including e.g. the composition of the nylon film-forming resin, the specific plasticizer employed, and the actual

processing temperatures involved.

Specific plasticizers that are preferred fall into three main categories, namely the long chain fatty acid amides, (i.e. those containing 16 to 18 carbon atoms in the chain), the aromatic sulfonamides, and the nylons and nylon copolymers which exhibit a melting point temperature of less than about $400^{o}F$ ($204^{o}C$). Within these categories, the most desirable plasticizers are lauramide, o,p-toluene-sulfonamide, N-ethyl-o,p-toluenesulfonamide (the two sulfonamides of course being mixtures of the ortho and para isomers), and nylons such as nylon 6/36, nylon 11 and nylon 12 having molecular weights of about 7,000 to 10,000. Other suitable products that can be used as plasticizing agents include nylon 11 and nylon 12 of about 25,000 molecular weight and melting at temperatures of about 370^{o} and $350^{o}F$ (188^{o} to $177^{o}C$), respectively, 2,2,4-trimethyl-1,3-pentane-diol, cumylphenyl-benzoate, and a product offered commercially by Paul and Stein Brothers of New York, New York under the designation STYSOLAK AW, referred to as a polyethylene oxide. STYSOLAK is believed to be a Registered Trade Mark.

The blends utilized to produce the first layer

of the oriented films of this invention may utilize what may be regarded as internally plasticized nylon rather than incorporating such a component as an independent third ingredient (i.e. in addition to a film-forming nylon and the EVOH copolymer). The internally plasticized nylons may be either random or block copolymers, or they may be alloys of a nylon resin with an alloying resin. In any event, it is believed that the comonomer or the alloying resin, as applicable, disrupts the crystalline structure of the relatively high melting nylon constituent and/or undergoes hydrogen or other secondary bonding so as to produce the desired effect. As will be appreciated, the ultimate objective is to provide a nylon ingredient which is processable at approximately the temperature at which the EVOH can be processed. Nylon copolymers that are suitable for use without added plasticizers include nylon 6/12; 6/36; and 6/66; the primary factor being that the copolymer has a melting point temperature below about 400°F (204°C). For some applications a low melting nylon (e.g. nylon 11 or nylon 12) can be used, without modification or added plasticizer, in combination with the EVOH. It may alternately be blended in virtually any proportion

with a higher melting nylon, such as nylon 6, to form the nylon component of the nylon/EVOH blend.

In producing the externally plasticized blends of the invention it will generally be desirable to premix the plasticizer with the film-forming nylon, so as to ensure maximum effectiveness in producing the desired result. This may be done in a compounding extruder or the like, depending to some extent on the physical state of the additive. It is generally most advantageous to produce pellets of such plasticized nylon, which can then be admixed with pellets of the EVOH prior to introduction into the extruder that is to be used for production of the first layer.

THE SECOND AND THIRD LAYERS

The second and third layers of the film serve generally the function of providing adhesion between the first layer and the fourth and fifth layers. Dispositionally, the second and third layers are located between the first and fourth layers and the first and fifth layers, respectively. As is clear from the above description of the first layer, and as will be clear from the following description of the fourth and fifth layers, the compositions of the first, fourth, and fifth layers can vary within

relatively broad ranges. Thus the examples which follow herein are considered illustrative, only, of the adhesive compositions and processes which are useful in making films of this invention. In general, the adhesive compositions are basically olefinic polymers or copolymers having carboxylic modifications thereto. The preferred basic polymers are LDPE, LLDPE, MDPE and EVA. The preferred carboxylic modification is an organic acid or anhydride, and more particularly maleic anhydride.

Specific adhesive polymers which have an LDPE as base polymer and which exemplify the desired compositions of the second and third layers, are Novatec AP220L available from Mitsubishi Chemical Industries Company, and PX-158-5, available from Chemplex Company. An LLDPE-based adhesive polymer is available from Mitsui Company, Japan, as Admer NF-500. Resins based on MDPE are Novatec AP212H and AP460H, for example. Resins based on EVA are Admer VF-500 from Mitsui Company, PX-3 and PX-100 from Chemplex Company, and CXA 3101 from DuPont Company. Another olefinic based resin containing vinyl acetate moieties is CXA E-136 from DuPont. In some cases it will be found advantageous to provide a blend of polymers as an adhesive layer. It may be a

blend of more than one of the adhesive polymers; it may be a blend of, for example, the selected adhesive polymer with material such as is incorporated into the adjacent layers. Indeed, it may be a blend of a combination of adhesive polymers and material substantially the same as that in the fourth or fifth layers. Thus it is conceivable that the second or third layer, or both, could comprise fractional amounts of polymeric material either identical to or very similar to those materials used in the compositions of the adjacent layers -- i.e. the first, fourth, and fifth layers, as applicable.

THE FOURTH AND FIFTH LAYERS

The fourth and fifth layers serve generally as the outer layers of the film. The compositions of the fourth and fifth layers at 40% to 100% EVA and 60% to 0% LLDPE. The fourth layer is generally designed to have heat sealable properties for the purpose of making a sealed container by means of heat seals. The fifth layer is disposed on the opposite surface of the film from the fourth layer, and in a formed container, serves as the outer layer of the container. In the formed container, the fifth layer serves a primary function of protecting the package and its product from physical abuse.

The compositions of the fourth and fifth layers may or may not be the same so long as each composition is within the compositional parameters given herein. The EVA provides high levels of adhesion at the interfaces of the fourth and fifth layers with the second and third layers. EVA polymers, particularly those having greater than 85% ethylene, also provide substantial structural strength to the film during the orientation process, and are especially beneficial for the orientation of tubular films. The ability of EVA to provide processing strength for the film manufacture is most efficiently used where high levels of EVA are present in the fifth layer. The LLDPE is highly desired for its capability of surviving intact the processes involved in shrinking those films which are formed into sealed containers and shrunk by a heat shrinking process. In general, the ability of, for example, a shrink bag to withstand the shrinking process correlates directly with increasing percent LLDPE, up to about 50% to 60% LLDPE.

Referring now to those film embodiments which are useful as shrink films, the inclusion of LLDPE in at least one of the fourth and fifth layers is preferred. Films having 25% to 40% LLDPE in at least one of the fourth and fifth layers show marked

improvements in shrink strength over films without LLDPE. Films having higher percentages of LLDPE, such as 40% to 60% in at least one of the fourth and fifth layers, have even better shrink performance, but are increasingly more difficult to stabilize in the manufacturing process, the degree of difficulty increasing with increased percentages of LLDPE. Because of manufacturing processes, layer compositions having greater than 60% LLDPE are not preferred.

The overall thickness of films of this invention is nominally the same as the thickness of conventional oriented films used for shrink packaging. Films are generally about 2.25 mils (0.06 mm) thick, with a normal range of 1.5 to 3.0 mils (0.04 to 0.08 mm). Films thinner than 1.5 mil (0.04 mm) tend to be too weak to perform all the required functions required of them. Films thicker than 3.0 mils (0.08 mm) are economically unable to compete with thinner, alternative films, though film thicknesses up to 8-10 mils (0.2 to 0.25 mm) will be functionally acceptable, and may be preferred where other specialized packaging properties are required.

Preferred thicknesses of the individual layers for a 2.25 mil (0.06 mm) film are as follows. The first layer is 0.15 to 0.30 mil (0.004 to 0.008 mm)

thick. The second and third layers are both about 0.10 mil (0.0025 mm), just thick enough to provide a continuous layer. The fourth layer is the thickest layer of the film and is 1.25 to 1.40 mil (0.03 to 0.0036 mm). The fifth layer is about 0.50 mil (0.01 mm).

LLDPE polymers suitable for use in the fourth and fifth layers are those having a melt index (MI) of up to about 6. Preferred LLDPE polymers have an MI of 0.5 to 1.5. Among the preferred polymers are DOW 2045, DOW XD-61508.01 and DuPont 11P. A modified LLDPE polymer, Admer NF-500, is also technically suitable, though its price usually prevents its use in the fourth and fifth layers.

EVA's preferred for use in the fourth and fifth layers are those having 6% to 12% vinyl acetate (VA) content and a melt index less than 1. While blend amounts are shown herein in weight percent, VA contents are mole percent. Especially preferred EVA's have VA content of 7% to 9% and melt index of 0.2 to 0.8.

While acceptable 3-layer subcombinations of the 5-layer films of the invention are difficult to make, as described hereinafter, the 5-layer films described herein surprisingly have been discovered

to be susceptible of being manufactured according to conventional orientation processes. Thus there appears to be a special cooperation among the layers of the 5-layer films that is not present in 3-layer films and 3-layer subcombinations of the 5-layer films. In the following examples a few films are described in detail as being manufactured using equipment common to the "double bubble" process. Films of the invention may be made by this process, or other conventional processes. Choice of the desired process depends not only on the film composition and structure but also on specific properties desired. In light of the disclosure herein, the choices on any particular film are now a matter of engineering selection.

Molecular orientation of the films of the invention may be effected utilizing any suitable technique, which depends somewhat on the structure of the film and the nature of the components of which it is comprised. It is believed that, in general, the most practical manner of extruding and orienting the film is by the so-called "double bubble" technique. As is well known, in such a method the film may be extruded downwardly as a tube formed by an annular die, and carried into a water quench tank, generally

with a cascade of water on the outside surface of the tube to provide initial cooling. The tube is flattened in the quench tank, is withdrawn from the quench tank, and is reheated (normally in a second water bath) to its orientation temperature. It is then stretched in the machine direction between two sets of rolls that are so rotated as to establish a linear rate differential therebetween, and is simultaneously oriented in the cross-machine direction as an inflated bubble trapped between the nips of the rolls. In accordance with conventional practice, the film is usually cooled by air in the orientation zone.

In the orientation process the film is typically stretched in both the machine direction and the cross machine direction. Convenient orientation ratios in both direcations are 2/1 to 4/1. Preferred orientation temperatures are 206°-212°F (97° - 100°C). While the temperature is adjusted in accordance with the film composition, a most preferred orientation temperature for many of the films of the invention is 210°F (98.9°C).

EXAMPLE 1

A mixture for use as the composition of the fourth and fifth layers is made by dry blending a

pellet mixture of 60% USI NA-235 EVA, and 40% UE-657 EVA. The composition of the first layer is SOARNOL-ET EVOH. The second and third layers are Novatec AP220L. A first extruder is charged with the SOARNOL-ET to form the first layer. Second and third extruders are charged with AP220L to form the second and third layers. Fourth and fifth extruders are charged with the blended EVA pellets to form the fourth and fifth layers. Using the five extruders, a five layer tube is downwardly coextruded. A water cascade cools the film initially as it exits the die. Cooling of the tube is completed in a water quench tank. The tube is then reheated to a temperature of 210°F (98.9°C), and is oriented as an inflated bubble at ratios of approximately 2.5/1 in the machine direction and 3.5/1 in the cross machine direction. The oriented film is cooled, the bubble collapsed, and the film wound up. In the resulting film the thicknesses are:

first layer - 0.15 mil (0.004 mm)
second layer - 0.10 mil (0.0025 mm)
third layer - 0.10 mil (0.0025 mm)
fourth layer - 1.40 mil (0.036 mm)
fifth layer - 0.50 mil (0.013 mm)

EXAMPLE 2

An oriented film is made as in EXAMPLE 1 except that the compositions of the first, fourth and fifth layers, and the thicknesses of the first and fourth layers are changed. The first layer is 0.30 mil (0.008 mm) thick and is a blend of 60% SOARNOL-E (EVOH) and 40% Custom 615I, nylon 6, made by dry blending the pellets as in the dry blending used for the composition of the fourth and fifth layers in EXAMPLE 1. The compositions for the fourth and fifth layers are prepared in like manner, and are 75% Norchem NPE-493 EVA and 25% DOW XD-61508.01 LLDPE. The thickness of the fourth layer is 1.25 mil (0.03 mm). The thickness of the fifth layer is the same as in EXAMPLE 1. The second and third layers are unchanged from EXAMPLE 1.

EXAMPLE 3

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Admer NF-500, LLDPE.

EXAMPLE 4

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Admer VF-500, EVA.

EXAMPLE 5

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Chemplex PX-3 EVA.

EXAMPLE 6

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Chemplex PX-158-5 LDPE.

EXAMPLE 7

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Chemplex PX-100 EVA.

EXAMPLE 8

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are DuPont CXA E-136 modified polyolefin.

EXAMPLE 9

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layersare DuPont CXA 3101 EVA.

EXAMPLE 10

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the first, fourth, and fifth layers are changed. The first

layer is 60% SOARNOL-ET EVOH and 40% UBE 5033B nylon 6/66 copolymer. The fourth and fifth layers are 75% USI UE-80232 EVA and 25% DOW XD-61508.01 LLDPE.

EXAMPLE 11

An oriented five layer film is made as in EXAMPLE 10 except that the compositions of the second and third layers are DuPont CXA E-136.

EXAMPLE 12

An oriented five layer film is made as in EXAMPLE 10 except that the compositions of the second and third layers are Novatec AP212H, MDPE.

EXAMPLE 13

An oriented five layer film is made as in EXAMPLE 10 except that the compositions of the second and third layers are Novatec AP460H, MDPE.

EXAMPLE 14

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Novatec AP212H, MDPE.

EXAMPLE 15

An oriented five layer film is made as in EXAMPLE 2 except that the compositions of the second and third layers are Novatec AP460H, MDPE.

EXAMPLE 16

An oriented five layer film is made as in

EXAMPLE 10 except that the thickness of the fifth layer is increased to 8.25 mils (0.21 mm) so that the finished thickness of the film is 10 mils (0.25 mm).

Table 1 shows data for each of the polymers used in the above examples.

TABLE 1

Polymer	Base Resin	VA Content	Melt Index
USI NA 235	EVA	4.5%	0.35
USI UE 657	EVA	12.0%	0.50
USI UE 80232	EVA	9.0%	0.40
NORCHEM NPE 493	EVA	8.0%	0.50
DOW XD-61508-01	LLDPE	NA	1.20
CUSTOM 615 I	NYLON 6	NA	3.19*
UBE 5033B	Nylon Copolymer	NA	----
NIPPON GOHSEI SOARNOL-E	EVOH	NA	5.50
NIPPON GOHSEI SOARNOL-ET	EVOH	NA	2.70
	Adhesive Polymers		
ADMER VF 500	vinyl acetate copolymer	----	2.20
DU PONT CXA 3101	vinyl acetate copolymer	----	3.50
DU PONT CXA E-136	Modified Polyolefin	yes	2.50
CHEMPLEX PX-3	EVA	9.0	3.00
CHEMPLEX PX-100	EVA	12.0	0.85
CHEMPLEX PX-158-5	LDPE	NA	1.80
NOVATEC AP220L	LDPE	NA	1.76
NOVATEC AP212H	MDPE	NA	0.70
NOVATEC AP460H	MDPE	NA	5.60
ADMER NF 500	LLDPE	NA	2.00

*Solution viscosity.

Films made according to EXAMPLES 2-11 were tested for layer adhesion on an Instron Tensile Tester at a cross-head speed of 10 inches per minute (25.4 cm/min). Test strips of film were cut six inches long by one inch wide (15.2 x 2.54 cm) with the length of the strips running in the machine direction of the film manufacturing process. Separation of the layers at their respective interfaces was initiated by one of two methods. In the first method, a piece of tape was adhered on each side of the film near the film edge and then the tapes were pulled apart. In the second method, the end of the sample strip was dipped into a solvent bath of 1, 1, 1, trichloroethane until the layers began to separate. The critical interlayer adhesions, those being the ones between the first and second layers, and between the second and fourth layers, are shown in Table 2 below. "Core"refers to the first layer. "Tie" refers to the second layer. "Inner" refers to the fourth layer.

Table 2

Example	Tie Layer	Layer Adhesion	
		Core/Tie (inner)	Tie/Inner
2	AP 220L	553	CNS
3	NF-500	785	CNS
4	VF-500	CNS	46
5	PX-3	760	CNS
6	PX-158-5	CNS	360
7	PX-100	115	CNS
8	CXA E-136	CNS	CNS
9	CXA 3101	88	CNS
10	AP 220L	CNS	CNS
11	CXA E-136	384	354

CNS = cannot separate. All specimens tore on Instron.

In a study of interlayer adhesions, three layer films were made wherein one of the surface layers was comprised of an adhesive polymer as in TABLE 1. The adhesive polymer layers were 0.6 mil thick (0.015 mm). The core layers were 0.3 mil thick (0.008 mm) and were comprised of 60% SOARNOL-E and 40% Emser F47 nylon 6. The other surface layer of the film was 1.35 mil thick (0.03 mm) and comprised 70%

EVA and 30% LLDPE.

In the first film, the adhesive polymer used for the second and third layers was CXA 3101. The film was hazy and tacky, and the resulting film had a wrinkly, non-uniform appearance. Though this film was considered unacceptable because of its appearance, it was tested for interlayer adhesion at the adhesive polymer layer interface. That adhesion was 74 grams.

In the second film, the adhesive polymer was Plexar 100. This film was processed satisfactorily, had an acceptable appearance and a favorable layer adhesion of 116 grams.

In a third film, the adhesive polymer was Plexar 3. This film was processed satisfactorily and had a good appearance, but the interlayer adhesion was only 34 grams, dramatically lower than the 760 grams attained in the comparable 5-layer film of EXAMPLE 5.

Regarding burst strengths of bags made from the films of the invention, it was expected that strengths would be related to the interlayer adhesions as shown in Table 2. For instance, the films of EXAMPLES 4 and 9 each have weak adhesion at one interface. It would be expected that

these films would be too weak to function normally such as for forming sealed containers. From past experience with 3-layer films, it is known that at least 100 grams, and preferably 300 grams, of adhesion is desired.

Sealed bag containers were fabricated from films of EXAMPLES 2-11 by making heat seals about the periphery of respective overlapping terminal edges. It was unexpectedly found that all the films of the examples formed good heat seals in forming sealed film packages by well-known heat sealing techniques. The films of all the examples herein could not be broken at pressures of 29 psi (2 bar). Packages made from film of EXAMPLE 12 were inflated to 45-55 psi (3.1 to 3.8 bar) before the seals failed.

As a comparison, a three layer oriented film having the structure EVA/EVOH/EVA was prepared and tested. The EVOH layer was 0.2 mil (0.005 mm). The EVA layers were 0.6 mil (0.015 mm) and 1.45 mils (0.037 mm) thick, for an overall film thickness of 2.25 mils (0.06 mm), the same thickness as in EXAMPLES 2-11. Thirty bags were tested in each of two bag sizes, 14" x 28" (35.6 x 71.1 cm) and 22" x 36" (55.9 x 91.4 cm). The range of burst

strengths were 19-25 psi (1.3 - 1.7 bar) for the smaller bags and 18-24 psi (1.2 - 1.6 bar) for the larger bags, the average burst strengths being 22.65 psi (1.56 bar) and 20.73 psi (1.43 bar) for the respective bags.

Regarding clip cut performance, bags made from the films of EXAMPLE 10 were tested on four clipping machines in a trial in a commercial plant. Clipping pressures and spikes were:

Machine No.	Clip Pressure		Spike	
	psi	bar	psi	bar
1	1350	93.0	60	4.1
2	1400	96.5	25	1.7
3	1425	98.2	50	3.4
4	1475	101.6	25	1.7

Out of 381 packages processed, only 4 packages were unacceptable because of clip cuts, for a highly satisfactory reject rate of 1%. Laboratory clipping trials on three-layer films of the structure /EVA/EVOH/EVA/, wherein EVOH included several EVOH blends, showed a wide range of clip cut failures at 1700 psi (117 bar) clip pressure, 100 psi (6.89 bar) spike; on the smaller bag. Average clip cut failure for 24 varieties of 3-layer structure was 66%. On the larger bags, the average failure rate is expected to

approach 100%.

One of the films in the above iterated clipping trials on 3-layer films had a core layer composition of 50% EVOH and 50% nylon. Its clip cut failure rate was 33%, whereas the failure rate for the five layer structure was 1%. Thus the addition of the second and third adhesive layers, while it did not always provide strong interlayer adhesion after the orientation process, it did provide uniformly strong heat seals, and excellent clip cut resistance.

In another plant trial, bags made from the films of EXAMPLE 10 were loaded with beef, sealed closed and heat shrunk. The bags had excellent seal properties. (The particular line on which the bags were tested had been experiencing a normal leaker rate of 8% to 15% using conventional bags having a three layer structure of /EVA/Saran/EVA/.) After being filled with meat, the bags were evacuated, heat sealed by a heat sealing bar, and heat shrunk at 200^{o}F (93^{o}C), all according to the normal operational practice on that line. In a test run of 1000 experimental bags made according to EXAMPLE 10, the leaker rate was only 4.5%.

The description herein has emphasized heat

shrinkable films, and particularly those associated with meat packaging. The films of the invention may also be fabricated with use of a thermal operation known generally as "heat setting", wherein, after the film is oriented, it is held under moderate tension at an elevated temperature of about 210°F (98.9°C) for about 2 to 10 seconds whereby the elastic memory of the film is relieved and the film loses its heat shrinking capability. Such films are dimensionally relatively stable at elevated temperatures. Such films may be preferred in packaging end use where heat shrinkage of the film is not preferred.

In making a bag, it is entirely satisfactory to start with a sheet of film and fold it over onto itself, with the fourth layer to the inside, and form heat seals along the terminal edges of the two opposite open sides to effect fabrication of a bag open at one end for insertion of the product. After the product has been inserted, the closing and sealing operation is the same as for a bag formed from tubular film.

While the films herein have been described as being preferential for use as a bag, they may be used as sheet film as well.

Also it is completely acceptable, and within the realm of the invention, to utilize the films described herein as a subassembly of a more complex film. Other layers may be adhesively mounted thereto. Particularly with regard to the heat set films, other layers may be added by thermal processes such as extrusion laminating, extrusion coating or combining at a nip with a combination of heat and pressure.

It will be appreciated that the second and third layers need not be identical in composition, nor need the fourth and fifth layers be identical in composition.

In this specification, percentages are by weight unless indicated otherwise.

Claims:

1. An oriented film comprising five polymeric layers including:

(a) a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol;

(b) second and third adhesive layers each adhered to a respective one of the opposite surfaces of the first layer, the second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and

(c) fourth and fifth layers adhered to the second and third layers on the respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene;

the said layers each having been stretched in molecular orientation to substantially the same degree, and the said layers being adhered to each other directly at the respective interfaces without the use of additional adhesive materials;

the oriented film being susceptible of being

made into a closed and sealed container or bag by means of heat seals formed along terminal edges of adjacent superimposed sheets or portions of the film.

2. An oriented film according to claim 1, wherein the first layer is either a blend comprising 30% to 50% nylon and 70% to 50% ethylene vinyl alcohol, for example 40% nylon and 60% ethylene vinyl alcohol, or consists essentially of ethylene vinyl alcohol.

3. An oriented film according to claim 1 or claim 2, wherein the fourth and fifth layers comprise a blend of 10% to 60%, for example 25% to 40%, linear low density polyethylene and 90% to 40% for example 75% to 60% ethylene vinyl acetate.

4. An oriented film according to claim 1 or claim 2, wherein the fourth and fifth layers comprise an ethylene vinyl acetate or a blend of ethylene vinyl acetates.

5. An oriented film according to any of claims 1 to 4, wherein the compositions of said second and third layers are chosen from modified low density polyethylene, modified linear low density polyethylene, modified medium density polyethylene, modified ethylene vinyl acetate, and blends of the

aforesaid polymers and copolymers.

6. An oriented film according to any preceding claim, wherein the composition of at least one of the said second and third layers includes a fractional amount of polymeric material either identical or very similar to, the materials used in the composition of at least one of the layers adjacent said at least one of the said second and third layers.

7. A method of making a five layer oriented polymeric film, wherein the film includes a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol; second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and fourth and fifth layers adhered to said second and third layers on their respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene; and wherein the method comprises the steps of:

(a) coextruding the five layers as a five layer film;

(b) cooling the film;

(c) reheating the film to molecular orientation temperature;

(d) molecularly orienting the film; and

(e) cooling the molecularly oriented five layer film;

the oriented film being susceptible to being made into a closed and sealed container by means of heat seals formed along terminal edges of adjacent superimposed sheets or portions of the film.

8. A method of making a five layer oriented polymeric film, wherein the film includes a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol; second and third adhesive layers adhered to said surfaces of said first layer, said second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and fourth and fifth layers adhered to said second and third layers on their respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene and wherein the method comprises the steps of:

(a) coextruding the five layers as a five layer film;

(b) cooling the film;

(c) reheating the film to molecular orientation temperature;

(d) molecularly orienting the film;

(e) heat setting the molecularly oriented film; and

(f) cooling the molecularly oriented film.

9. A method according to claim 7 or claim 8, wherein the film is coextruded in the shape of a tube and is oriented by introducing into said tube a pressurized gas and drawing the tube between two nips having a differential rate of drawing speed therebetween, such that the pressure of the gas and the drawing of said nips effect the molecular orientation of the film as an expanded tube.

10. A method according to claim 7, 8 or 9, wherein the first layer is chosen from a blend of 30% to 50% nylon and 70% to 50% ethylene vinyl alcohol, for example 40% nylon and 60% ethylene vinyl alcohol, or consists essentially of ethylene vinyl alcohol.

11. A method according to any of claims 7 to 10, wherein the fourth and fifth layers are formed from blends of 10% to 60%, for example 25% to 40%, linear low density polyethylene and 90% to 40%, for

example 75% to 60% ethylene vinyl acetate.

12. A method according to any of claims 7 to 11, wherein the compositions of said second and third layers are chosen from modified low density polyethylene, modified linear low density polyethylene, modified medium density polyethylene, modified ethylene vinyl acetate, and blends of the aforesaid polymers and copolymers; the compositions of said fourth and fifth layers preferably comprising blends of 25% to 40% linear low density polyethylene and 75% to 60% ethylene vinyl acetate.

13. A fabricated plastics container or bag having an opening on one edge thereof, the bag having been fabricated from an oriented film comprising five polymeric layers, including:

(a) a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol;

(b) second and third adhesive layers each adhered to a respective one of the surfaces of the first layer, the second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and

(c) fourth and fifth layers adhered to said second and third layers on the respective surfaces opposite said first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene;

the said layers each having been stretched in molecular orientation to substantially the same degree, and the said layers being adhered to each other directly at their interfaces without the use of additional adhesive materials; and the bag being susceptible to being made into a closed and sealed container by means of a heat seal along the said opening.

14. A bag according to claim 13, fabricated from said film which is produced in the form of a tube, the bag being formed by heat sealing a length of said tube along one open end leaving the other end open, the bag being closed along said other end by heat sealing after filling.

15. A bag according to claim 13, fabricated from two superimposed sheets or portions of said film and appropriately heat sealed peripherally to form a pouch open along one edge to permit filling,

the pouch being subsequently heat sealed along the said one edge to close the bag.

16. A bag according to claim 13, 14 or 15, wherein the first layer is either 30% to 50% nylon and 70% to 50% ethylene vinyl alcohol, for example 40% nylon and 60% ethylene vinyl alcohol, or consists essentially of ethylene vinyl alcohol.

17. A bag according to claim 13, 14, 15 or 16 wherein the fourth and fifth layers comprise blends of 10% to 60%, for example 25% to 40% linear low density polyethylene and 90% to 40%, for example 75% to 60% ethylene vinyl acetate.

18. A bag according to any of claims 13 to 17, wherein the compositions of the second and third adhesive layers are chosen from modified low density polyethylene, modified linear low density polyethylene, modified medium density polyethylene, modified ethylene vinyl acetate, and blends of the aforesaid polymers and copolymers.

19. A method of fabricating a plastic bag having an opening on one edge thereof susceptible of closure by heat sealing, the remainder of the periphery of the bag having been closed as appropriate by one or more heat seals to form an open ended pouch, the said bag being fabricated from an oriented

film which includes a first barrier layer having a composition of 0% to 50% nylon or nylon copolymer, and 100% to 50% ethylene vinyl alcohol; second and third adhesive layers adhered to respective surfaces of the first layer, the second and third adhesive layers both comprising olefinic polymers or copolymers having carboxyl modifications thereto; and fourth and fifth layers adhered to the second and third layers on their respective surfaces opposite the first layer, the fourth and fifth layers comprising 40% to 100% ethylene vinyl acetate and 60% to 0% linear low density polyethylene; and the method including the steps of:

(a) coextruding the five layers as a five layer film;

(b) cooling the film;

(c) reheating the film to molecular orientation temperature;

(d) molecularly orienting the film;

(e) cooling the molecularly oriented five layer film; and

(f) forming one or more heat seals as appropriate at the periphery of said bag except along the said one edge.

20. A method according to claim 19 and

including, after step (d), and before step (e), the additional step of heat setting the oriented film by holding it at an elevated temperature of 200° to 250°F (93.3° to 121°C) for 2 to 10 seconds.

21. A method according to claim 19 or claim 20, wherein the first layer either comprises a blend of 30% to 50% nylon and 70% to 50% ethylene vinyl alcohol or consists essentially of ethylene vinyl alcohol.

22. A method according to claim 19, 20 or 21, wherein the fourth and fifth layers comprise a blend of 25% to 40% linear low density polyethylene and 75% to 60% ethylene vinyl acetate.

23. A method according to claim 19, 20, or 21, wherein the compositions of the second and third adhesive layers are chosen from modified low density polyethylene, modified linear low density polyethylene, modified medium density polyethylene, modified ethylene vinyl acetate, and blends of the aforesaid polymers and copolymers; and the compositions of the fourth and fifth layers preferably comprise blends of 25% to 40% linear low density polyethylene and 75% to 60% ethylene vinyl acetate.

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EUROPEAN SEARCH REPORT

0141555
Application number

EP 84 30 6979

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)
X	EP-A-0 087 080 (KUREHA KAGAKU KOGYO KABUSHIKI KAISHA) * claim 1; page 10, line 25 - page 11, line 6; page 12, line 5 - page 13, line 2; page 13, line 12 - page 14, line 7 *	1,2,3, 5,7,9, 10,11-15,17-19,22, 23	B 32 B 27/08 B 65 D 30/08 B 65 D 65/40
Y		1,2,4, 6,8,20	

P,D	EP-A-0 092 897 (AMERICAN CAN COMP.) * abstract; figure 3; claims 1-5,7-9,13-16; page 9, lines 12-16; page 14, line 8 - page 15, line 5; page 18, lines 1-4; page 17, line 11; page 22, line 25 *	1,2,3, 5,7,9-19,21-23	TECHNICAL FIELDS SEARCHED (Int. Cl.4) B 32 B
Y		4	

Y,D	US-A-4 247 584 (WIDIGER et al.) * abstract; figures; example 2; claims 7,11,12,15,16,19,34-37,39-43; column 4, lines 15-34 *	4	
	--- -/-		

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-12-1984	DE LA MORINERIE B.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	EP-A-0 064 330 (AMERICAN CAN COMP.) * abstract; claims 1,6,12,13; example 4; page 6, line 9 - page 7, line 18; page 15, line 9 - page 16, line 1 * ---	1,2	
Y	EP-A-0 063 006 (AMERICAN CAN COMP.) * claims 1,5,6,8,10-15,21; page 12, lines 2-10 * ---	1	
Y	GB-A-1 567 189 (TORAY IND. INC.) * claims 1,4,8,9,12,15,18,20,26-28,33-35 * ---	8,20	
A	EP-A-0 084 421 (TOYO SEIKAN KAISHA LIM.) * figures 5-7; claims 5,9,11-13; page 37, line 7 - page 38, line 22 * ---	1,5,2	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
A	GB-A-2 006 108 (TOYO SEIKAN KAISHA LTD.) * figure 2; claims 1,7; table 2, blend 1; page 7, line 61 - page 8, line 3 * --- -/-	1,6	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-12-1984	DE LA MORINERIE B.M.

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Application number

EP 84 30 6979

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	GB-A-2 048 209 (TOYO SEIKAN KAISHA LTD.) * abstract; figure 3; claims; page 2, line 56 - page 3, line 10; page 5, lines 1-37 * ---	6	
A	GB-A-2 113 696 (GETTY CHEMICAL COMP.) * abstract; claims * -----	1,5,6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-12-1984	DE LA MORINERIE B.M.

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